

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	September 1998	Final: 3/1/95-2/28/98	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Structure, Morphology, and Transport Relationships in Segmented Polyurethanes: A Molecular Simulation Approach		Contract No. DAAH04-95-1-0125	
6. AUTHOR(S) William J. MacKnight Samuel P. Gido Shaw Ling Hsu		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Polymer Science and Engineering Department University of Massachusetts Amherst, MA 01003-4530		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 33784.9-CH	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) In the last funding period, we continued to focus on the formation of polyurethanes by controlling the relative kinetics of crosslinking versus phase separation of hard segments. These materials exhibit interesting mechanical behavior and controllable barrier properties. A series of polyurea urethanes was isothermally synthesized from toluene diisocyanate (TDI), water, and trifunctional poly(propylene oxide) in the temperature range of 50 - 150 °C. Morphologies of the samples vary significantly as a function of reaction temperature. In this system, phase separation competes with polymerization and crosslinking. Both transmission electron microscopy and atomic force microscopy have displayed a network type structure for the 50 °C samples; the 150 °C samples appear to be homogeneous. Infrared analysis reveals that samples prepared at 150 °C possess a morphology that is less strongly hydrogen bonded and with a broader distribution of hydrogen bonded states in comparison to those prepared at lower temperatures. From this combination of techniques, it can be inferred that phase separation occurs more rapidly than crosslinking at low temperatures; consequently, a phase separated morphology results. In contrast, crosslinking occurs more rapidly than phase separation at higher reaction temperatures.			
14. SUBJECT TERMS polyurethanes, AFM, atomic force microscopy, phase separation, crosslinking			15. NUMBER OF PAGES 1
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

**STRUCTURE, MORPHOLOGY, AND TRANSPORT RELATIONSHIPS IN
SEGMENTED POLYURETHANES:
A MOLECULAR SIMULATION APPROACH**

FINAL REPORT

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CONTRACT DAAH04-95-1-0126**

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19990104 102

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The principal class of materials under consideration in this research is polyurethanes, copolymers consisting of alternating soft and hard segment units. The soft segment is generally a low molecular weight polyether; the hard segment consists of an aromatic diisocyanate condensed with a low molecular weight diol. Properly chosen components yield thermoplastic elastomers which exhibit high modulus, high extensibility, high barrier properties, and exceptional toughness. Development of such properties depends on the microphase segregation of the polyurethane into hard and soft segment rich regions of the polymer as well as organization of hard segments into some form of domain structure.^{1,2} One of the critical deficiency associated with such system is the instability at elevated temperatures. Therefore, in order stabilize the phase separated structures, covalent crosslinking is necessary. A series of polyurea urethanes was isothermally synthesized from toluene diisocyanate (TDI), water, and trifunctional poly(propylene oxide) in the temperature range of 50 - 150 °C. The amount of water controls the average hard segment length. Urethane linkages, which are created through reactions of isocyanates and hydroxyl endgroups, are the junction points between the polyether soft segments and the urea hard segments that arise from the amine/isocyanate reactions. In this system, phase separation competes with polymerization and crosslinking thus capable of generating a spectrum of structures ranging from completely phase separated systems to a nearly homogenous structure. Because of the versatility associated with such systems, a tremendous number of characterization studies have been carried out. Yet there have not been any successful observations to directly measure the most probable size of domain and their size distribution.

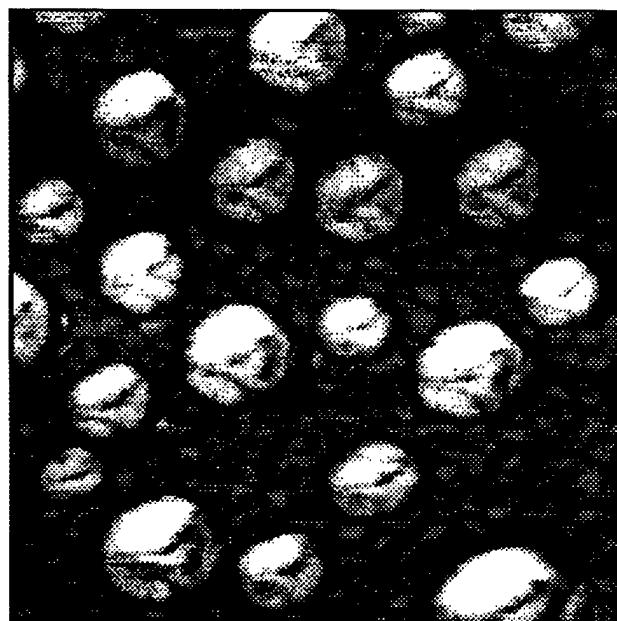
To make tough hole free solid films, we have compressed very small amounts of reacting material (15 g) in a steel mold (cross sectional diameter 15 cm) preheated to a specified temperature. Since the heat capacity of the mold is much larger than the amount of heat generated during the exothermic reaction, we have been able to maintain a constant temperature environment. By synthesizing thin films (0.9-1.3 mm) at various temperatures, we have been able to observe systematic changes in the final film morphology. Microstructures of polyurethanes have not been described accurately because none of the traditional characterization techniques offer a complete or coherent picture of polyurethane morphology. Thermal methods, such as differential scanning calorimetry (DSC), can provide information about crystallinity, glass transition temperature, or heat capacity. These polyurethane systems, however, generally do not crystallize and chemical crosslinks make T_g rather insensitive to changes in degree of phase separation. Scattering techniques such as x-ray and light scattering are useful only if the microstructural features are of the appropriate length scale. Moreover, x-ray requires sufficient electron density contrast for the features to be evident. In transmission electron microscopy, lack of contrast, as well as beam damage, can be a significant barrier in some systems.

Atomic force microscopy (AFM), can be used to analyze the phase separated morphology of our polyurethane system. Since its advent in 1986,³ the atomic force microscope has contributed to the characterization of many material surfaces. Much of the initial work dealt with topographical investigations. However, in recent years, other aspects of atomic force microscopy have become useful. In particular, phase imaging techniques have become areas of active investigations due to their ability to image viscoelastic properties of surfaces. It is this aspect of atomic force microscopy that we hope to exploit in our multi-phase polyurethane studies. In tapping mode used in our studies, the tip oscillates at its resonant frequency, typically 100-300 kHz. When the tip encounters a peak or valley on the surface, the scanner position adjusts to maintain a constant amplitude. Since the tip contacts or "taps" the surface only at the bottom of its swing, contact time is very brief and surface damage is abated. Movement of the cantilever/tip assembly can be described by basic mechanical vibration theory.⁴ Depending on chemical composition, the oscillating tip interacts with the sample surface to different extents. This interatomic interaction creates a phase shift between the input oscillation and the output signal. This phase angle relates to the amount of damping of the cantilever. Since each domain in a phase separated structure should have a different effective interatomic potential, a map of the phase shift represents chemical composition.

In a model system such as PS/PVME, the two components phase separate into well-defined rich and poor phases when the temperature rises above the Lower Critical Solution Temperature (LCST). The resulting morphologies in thin films of this blend have been characterized previously.⁵ We have prepared a thin film of a 60/40 blend by spin-casting it onto a silicon wafer and heating it to 160 °C, which is above the LCST for such a composition and molecular weight. A tapping mode image of the PS/PVME film is shown in the Figure. Diameters of the spherical domains are in the range of 250 nm. Bright areas represent PS poor phases; PS rich sections are shown as the darker matrix phase representing a direct observation of the morphology of this model blend.

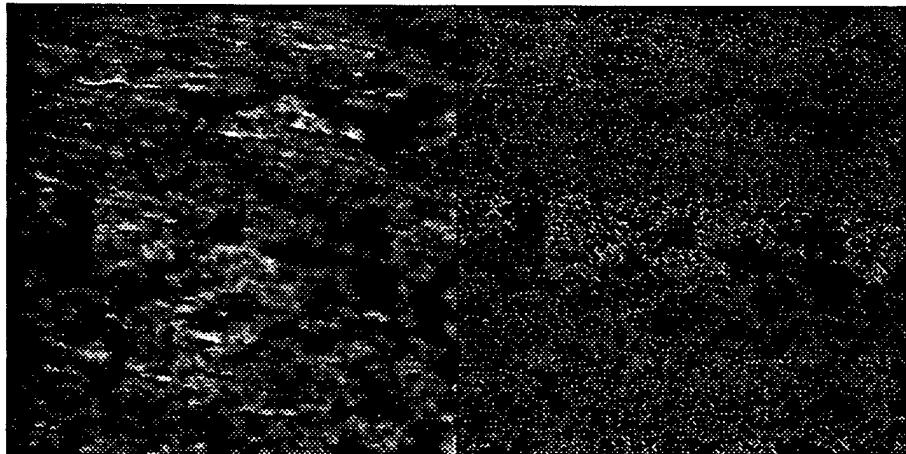
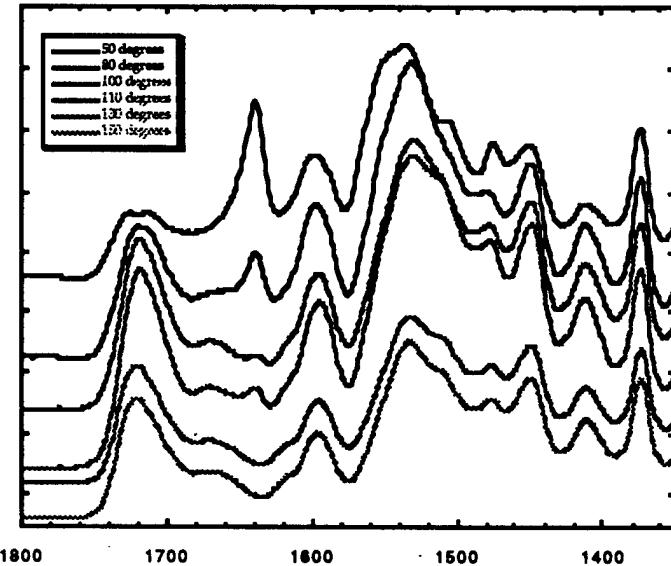
In the last funding period, for crosslinkable polyurethanes, we can infer that the relative kinetics of polymerization, crosslinking, and phase separation change as a function of temperature and that the competition between these processes can generate very different morphologies. As the system chemically crosslinks, mobility of polymer chains decreases and consequently hampers the phase separation process. The presence of strongly hydrogen bonded hard segments in the infrared spectra of samples prepared at 50 °C, along with the network-like structure shown in atomic force microscopy and transmission electron microscopy, indicate that a well phase separated structure forms at low temperatures. This

implies that a significant amount of phase separation has occurred before the sample gels. In contrast, the homogeneous morphology in atomic force microscopy and transmission electron microscopy and the absence of well-ordered hydrogen bonding in the ATR spectra for samples synthesized at 150 °C suggest that at high reaction temperatures, chemical crosslinking occurs faster than phase separation. The result is a system in which a phase separated morphology never develops, even though such a state is thermodynamically favored.



The three techniques that we have used, infrared spectroscopy, transmission electron microscopy, and atomic force microscopy yield a consistent picture. For the 50 °C sample, a phase separated structure, hydrogen bonded urea segments dominate. A manifestation of this interaction is a decrease in vibrational frequency of the infrared active urea carbonyl band (a well-defined absorption peak at 1640 cm⁻¹).^{6,7} This has been attributed to a urea carbonyl that is hydrogen bonded to two N-H groups of another urea segment. Since effective hydrogen bonding is highly directional, well-defined infrared spectroscopic features such as this can be observed only in samples with a high degree of packing order. Samples prepared at 150 °C show no evidence of a peak at 1640 cm⁻¹; instead, there is a broad peak centered at 1660 cm⁻¹. The expansive band at 1660 cm⁻¹ was assigned to a hydrogen bonded urea carbonyl that does not have the ordered three dimensional structure represented by the 1640 cm⁻¹ band.⁸

The AFM image of the same sample is shown in the Figure. It is clear that the domains can be seen clearly. In contrast the samples prepared at higher temperatures exhibit a nearly homogeneous structure. These differences are not only important in the determining mechanical properties but their transport properties as well.



References

- (1) Tao, H.-J.; Hsu, S. L.; MacKnight, W. J. *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)* 1992, 33(2), 575.
- (2) Tao, H. J.; MacKnight, W. J.; Hsu, S. L. *Macromolecules* 1994, 27, 1720.
- (3) Binnig, G.; Quate, C. F.; Gerber, C. *Phys. Rev. Lett.* 1986, 56, 930-933.
- (4) Winkler, R. G.; Spatz, J. P.; Sheiko, S.; Moller, M.; Reineker, P.; Marti, O. *Phys. Rev. B* 1996, 54, 8908-8912.
- (5) Reich, S.; Cohen, Y. *J. Polym. Sci., B, Polym. Phys.* 1981, 19, 1255-1267.
- (6) Coleman, M. M.; Sobkowiak, M.; Pehlert, G. J.; Painter, P. C.; Iqbal, T. *Macromol. Chem. Phys.* 1997, 198, 117-136.
- (7) Ishihara, H.; Kimura, I.; Saito, S.; Ono, H. *J. Macromol. Sci. Phys.* 1974, B10, 591-618.
- (8) Sung, C. S. P.; Smith, T. W.; Sung, N. H. *Macromolecules* 1980, 13, 117-121.

List of Publications

1. "Investigation of the Phase Separation Behavior of Polyurethane Elastomers by Two-Dimensional Wide-Line-Separation Nuclear Magnetic Resonance Spectroscopy" *Macromolecules* **28**, 4036-4038 (1995) (Hun-Jan Tao, David M. Rice, William J. MacKnight and Shaw L. Hsu)
2. "The Effect of Polymer Structures on the Ionic Association of LiClO₄ in Polyether-Based Network Polymer Electrolytes Studied by FT-Raman Scattering Spectroscopy" *J. Electrochem. Sci.* **142**, L205-L207 (1995) (H. Akashi, S.L. Hsu and W.J. MacKnight)
3. "End-Group Effect on Chain Conformation of Poly(propylene glycol) and Poly(ethylene glycol)" *J. Appl. Polym. Sci.* **64**, 197-202 (1997) (with Shunghoe Yoon, William J. MacKnight and Shaw Ling Hsu)
4. "Spectroscopic Evaluation of Models for Polyelectrolyte Chain Conformation in Dilute Solution" *Macromolecules* **29**, 7514-7520 (1996) (with Wanda J. Walczak, David A. Hoagland and Shaw L. Hsu)
5. "Raman Analysis of a Conformational Distribution of Poly(ethylene oxide) and Its Model Compound in the Liquid State" *Macromolecules* **30**, 3796-3802 (1997) (with Xiaozhen Yang, Zhaohui Su, Dacheng Wu, Shaw Ling Hsu and Howard D. Stidham)

List of All Participating Scientific Personnel and Degrees Awarded

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